as in the case of monatomic gases. Its atomic diameter, deduced from the viscosity of the gas, is $3{\cdot}13 \times 10^{-8}$ cm., which makes its mean area $S = 0{\cdot}78 \text{ cm}^2 \times 10^{-15}$. This is considerably larger than any of the values of $\bar{A}$ for neon (Table II), and points to the fact that a nitrogen molecule does not resemble two linked neon atoms. In this negative sense, therefore, we again have corroboration of Langmuir's theory. For both points of view indicate that, whatever may be the actual arrangement of the nitrogen molecule, its mode of formation from two atoms is essentially different from that of its neighbour, the oxygen molecule.

13. In conclusion, I wish to express my gratitude to Prof. S. Chapman for reading the draft of this paper, and for making the suggestion—already referred to—which I have adopted.

On the Similarity between Carbon Dioxide and Nitrous Oxide.

By A. O. Rankine, D.Sc., Professor of Physics in the Imperial College of Science and Technology.

(Communicated by Prof. H. L. Callendar, F.R.S. Received October 30, 1920.)

1. One of the most remarkable evidences in favour of the Lewis-Langmuir[*] theory of molecular constitution is the close degree of equality between nearly all of the physical constants of the two compounds, carbon dioxide and nitrous oxide. This identity is attributed by Langmuir to the arrangement of external electrons being the same for the molecules of the two gases in question. It is the purpose of the present communication to show that an appeal to the kinetic theory of gases, in conjunction with what is now known from W. L Bragg's[†] work regarding the dimensions of atoms, produces substantial additional evidence in support of the Lewis-Langmuir views. In particular, it will be shown that the molecules of CO_2 and N_2O behave not merely as though they had the same size and shape, but as if each of them had an external electron arrangement practically the same as that of *three neon atoms in line and contiguous.*

2. This arrangement is precisely that which Langmuir suggests and is represented in fig. 1. A single neon atom is pictured as having eight outer

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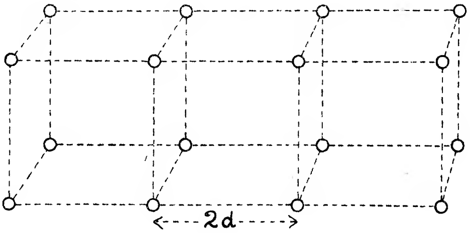
[*] I. Langmuir, 'Journ. Amer. Chem. Soc.,' vol. 41, p. 868 (1919).

[†] W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169 (1920).

electrons, presumably at the corners of a cube. Other atoms, although deficient in outer electrons, can, by forming molecules in which electrons are shared, attain a stable but multiple neon arrangement. Thus, if fig. 1 be taken to represent the molecule N_2O, it can be readily seen that the necessary conditions are fulfilled. The total deficiency of outer electrons is 8 (3 for each N atom and 2 for the O atom), and there are thus $24-8=16$ only available. These serve exactly to complete the arrangement shown, which is like three neon atoms with two faces shared. On the other hand, if the molecule is CO_2, the electron deficiency is again 8 (2 for each O atom and 4 for the C atom), and the same arrangement therefore serves. There is no need, for our present purpose, to distinguish which cube represents any particular atom. The distribution of electrons is, according to Langmuir, externally equivalent to three neon atoms joined together, and is the same for both CO_2 and N_2O.



Arrangement of outer electrons in the molecules CO_2 and N_2O. (after Langmuir)

FIG. 1.

3. The data which W. L. Bragg (*loc. cit.*) has derived from X-ray crystal measurements enable us to specify how far apart are the centres of two neon atoms when they are brought so close together that their outer electron shells are contiguous. The distance in question is given by him as $1{\cdot}30 \times 10^{-8}$ cm. It is now proposed to construct a hypothetical molecule of three neon atoms with their centres in the same straight line, and successive centres $1{\cdot}30 \times 10^{-8}$ cm. apart, and compare its kinetic behaviour with that of the molecules of CO_2 and N_2O. The degree of correspondence will determine to what extent Langmuir's model is a correct representation of fact. The method employed is the natural outcome of that described by the author* in a previous paper, in which, among other things, the molecule O_2 was compared with two adjacent neon atoms. A single neon atom behaves, according to the kinetic theory of gases, like a hard elastic sphere which comes periodically

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* A. O. Rankine (preceding paper).

into collision with other neon atoms. The diameter of this hard sphere, calculated by means of Chapman's* formula, and using the only available viscosity data,† proves to be $2 \cdot 35 \times 10^{-8}$ cm. This is considerably in excess of the distance $1 \cdot 30 \times 10^{-8}$ cm., which measures the distance between the centres of two neon atoms which are sharing outer electrons. Consequently, the hard spheres, to which each atom is separately equivalent from the point of view of mutual collision, will overlap in the manner indicated in fig. 2, which represents the three neon atoms we are considering, with

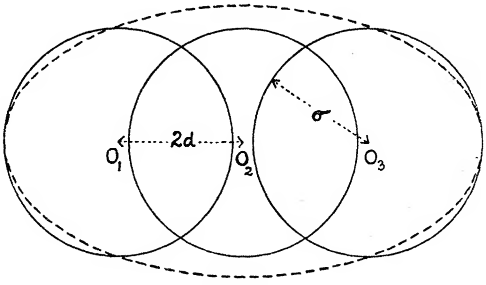

Fig. 2.

$2d = 1 \cdot 30 \times 10^{-8}$ cm., and $2\sigma = 2 \cdot 35 \times 10^{-8}$ cm. In applying the kinetic theory of gases to this hypothetical molecule we have, therefore, to recognise the molecule as not being spherical, and to estimate its collision frequency on this new basis. Put in another way, we have to find the average area, presented as a target by such a molecule, in terms of the corresponding area ($\pi\sigma^2$) for a single neon atom. This mean area we can then compare with the actual mean areas of the molecules of CO_2 and N_2O, as deduced from their viscosity data.

4. In my former paper, already referred to, I have made this calculation in the case of two equal overlapping spheres, treating them, as a first approximation, as a hard elastic body of that shape. If we denote by $\bar{A}$ the mean area presented by this body for all possible orientations of the axis, it was shown that

$$\bar{A} = \pi\sigma^2 + \pi\sigma^2 \cdot \frac{4}{3\pi}\left\{\left(\frac{1}{K} + K\right)\mathbf{E}\left(K, \frac{\pi}{2}\right) - \left(\frac{1}{K} - K\right)\mathbf{F}\left(K, \frac{\pi}{2}\right)\right\}, \quad (1)$$

where $K = \frac{d}{\sigma} < 1$, and $\mathbf{F}\left(K, \frac{\pi}{2}\right)$ and $\mathbf{E}\left(K, \frac{\pi}{2}\right)$ are complete elliptic integrals of the first and second kinds, respectively.

The right-hand side of (1) is evidently made up of two parts: the first, $\pi\sigma^2$, being the complete area of projection of one of the spheres; and the second part, which we will denote by $\bar{X}$, being the mean area of the crescent formed by the variable overlapping of the two spheres. If there are n equal spheres, equally spaced in a straight line, there will be $n-1$ crescents exactly similar—for a given orientation—to that just described. Consequently, the total mean area presented will be

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* S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1916).

† A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 84, p. 181 (1910).

$$\pi\sigma^2+\overline{n-1}\,\bar{X}.$$

It is thus very easy to pass from the case of two spheres to that of any number equally spaced in line. In our present case the number $n = 3$, and the mean area, $\bar{B}$, becomes

$$\bar{B} = \pi\sigma^2\left[1+\frac{8}{3\pi}\left\{\left(\frac{1}{K}+K\right)\mathbf{E}\left(K,\frac{\pi}{2}\right)-\left(\frac{1}{K}-K\right)\mathbf{F}\left(K,\frac{\pi}{2}\right)\right\}\right]. \quad (2)$$

Using the values of d and σ, already given as applicable to neon, we find that the mean area, which would be presented as a target by the hypothetical molecule contemplated, is

$$\bar{B} = 0{\cdot}895\times10^{-15}\ \text{cm.}^2. \quad (3)$$

5. An alternative model of the shape of the molecule has also been considered, namely, to treat it as an ellipsoid of revolution,* having its major axis coincident with the axis of the three spheres, as indicated by the dotted line in fig. 2. The results obtained for the mean area presented are

$$(a)\ 0{\cdot}951\times10^{-15}\ \text{cm.}^2,$$

and

$$(b)\ 0{\cdot}853\times10^{-15}\ \text{cm.}^2,$$

according as we take the volume of the spheroid as being equal to that of the three spheres, or to their total volume less the common portions. The dotted line in fig. 2 shows the principal section of the first of these spheroids; the second spheroid lies close inside, its minor axis being 0·91 of the first. The justification for substituting a spheroid for the three spheres does not appear to be so great as when there are merely two spheres, and it seems reasonable to rely on the value of $\bar{B}$ as given in (3) rather than on the alternatives (a) and (b), especially as $\bar{B}$ is the intermediate value. The comparison will therefore be carried out on this basis.

6. We have now to consider the actual values of the mean areas presented as targets by the molecules of N_2O and CO_2. Chapman's (*loc. cit.*) formula may be used for the estimation of this mean area (which we will denote by $\bar{S}$), provided we know, in addition to the density of the gas, the number of

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* The treatment of this problem differs in no essential way from that given in my former paper, and need not be repeated here. The magnitudes of the major and minor axes have merely to be determined on the new condition that there are three spheres instead of two.

molecules per cubic centimetre at N.T.P., the viscosity at a definite temperature, and the mode of variation of viscosity with temperature. For the densities of the two gases I have used the values corresponding to their molecular weights, the departures from "perfect gas" behaviour being negligible. For the number of molecules per cubic centimetre at N.T.P., Millikan's* modern value, $2{\cdot}705 \times 10^{19}$, has been adopted. The viscosity data are more uncertain. There is little doubt about the absolute values of the viscosity (η_0) at 0° C., but Sutherland's† constants (C) are not known with accuracy. I have relied, as far as possible, on modern determinations, and have taken for CO_2 the value $\eta_0 = 1{\cdot}384 \times 10^{-4}$ C.G.S., which is the mean of Breitenbach's‡ estimate, $1{\cdot}388 \times 10^{-4}$ and Vogel's,§ $1{\cdot}380 \times 10^{-4}$. For N_2O the value used is Vogel's, $\eta_0 = 1{\cdot}362 \times 10^{-4}$ C.G.S. Only Von Obermayer's‖ data are available for the calculation of C for the latter gas, and the value thus obtained is $C = 260$. In the case of CO_2 there have been several investigations of the variation of viscosity with temperature, the principal ones being Holman's,¶ Von Obermeyer's, and Breitenbach's. The latter gives the value $C = 239$, and this is supported by calculations from Von Obermayer's figures. On the other hand, Sutherland obtains the value $C = 277$ from Holman's data. The estimate I have used is $C = 249$, which is the same as that adopted by Chapman (*loc. cit.*), but it is evident that some uncertainty still exists.

On the basis of the above data, the values obtained for the mean target areas of the molecules of the two gases are:—

$$CO_2, \quad \bar{S} = 0{\cdot}870 \times 10^{-15} \text{ cm.}^2,$$

$$N_2O, \quad \bar{S} = 0{\cdot}867 \times 10^{-15} \text{ cm.}^2.$$

Too much stress must not be laid on the precision of the equality of these two figures. Each is quite possibly subject to an error of something like 5 per cent., on account of uncertainty regarding Sutherland's constant. Within the limits of experimental error, however, the molecules of CO_2 and N_2O do behave, in the gaseous state, as though they were of identical size and shape.

7. The comparison of $\bar{S}$ with the mean target area, $\bar{B}$, of the hypothetical triple neon molecule is shown in the following Table.

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* R. A. Millikan, 'Phil. Mag.,' vol. 34, p. 1 (1917).

† W. Sutherland, 'Phil. Mag.,' vol. 36, p. 507 (1893).

‡ P. Breitenbach, 'Ann. der Physik,' vol 5, p. 166 (1901).

§ H. Vogel, 'Berlin Diss.' (1914).

‖ A. von Obermayer, 'Sitz. Akad. Wien,' vol. 73, p. 433 (1876).

¶ S. Holman, 'Phil. Mag.,' vol. 21, p. 199 (1886).

Table I.—All areas in $\text{cm.}^2 \times 10^{-15}$.

Gas.	$\bar{S}$.	$\bar{B}/\bar{S}$.
Carbon dioxide	0·870	1·03
Nitrous oxide	0·867	1·03
$\bar{B} = 0{\cdot}895$		

In both cases the ratio $\bar{B}/\bar{S}$ is seen to differ by only 3 per cent. from unity. We can, therefore, conclude that not only have the molecules CO_2 and N_2O the same molecular dimensions, but that their behaviour is, within the limits of experimental error, consistent with the assumption that in both cases the dimensions are those of three neon atoms in line with contiguous outer electron shells.

Experiments on Electron Emission from Hot Bodies.

By Sih Ling Ting, M.Sc., Birmingham.

(*Communicated, with a Preface, by* Prof. O. W. Richardson, F.R.S.)

(Received May 6, 1920.)

PREFACE.

The first measurements* of the kinetic energy of the electrons emitted from hot bodies were made by myself, partly in collaboration with Dr. F. C. Brown, in 1907–1909. The completed experiments were practically confined to platinum as a source of emission, largely on account of technical difficulties experienced with other materials. These experiments showed that the velocity distribution among the emitted electrons was in close agreement with Maxwell's law of distribution for a gas, of molecular weight equal to that of the electrons, in thermal equilibrium at the temperature of the source. This applies both to the component of velocity normal to the emitting surface and to that in a perpendicular direction. In the simple unidimensional case, where the cathode and anode form parallel planes of indefinite extent, the current, i, which flows against a retarding potential, V,

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* 'Phil. Mag.,' vol. 16, pp. 353, 890 (1908); vol. 18, p. 681 (1909).